

JAPANESE PATENT PUBLICATION (A)

(11)Publication number : **61-076502**

(43)Date of publication of application : **19.04.1986**

(51)Int.CI.

C08B 37/06

(21)Application number : **59-198334** (71)Applicant : **mitsubishi acetate
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(54) METHOD FOR PRODUCING PARTIALLY AMIDATED PECTIN

SPECIFICATION

1. TITLE OF THE INVENTION

Method for Producing Partially Amidized Pectin

2. CLAIMS

1. A method for producing a partially amidized pectin comprising causing a pectin-containing plant in a dry state to swell by an acid to partially demethoxylate the pectin, then dissolving the pectin and separating the insolubles, then causing the pectin to precipitate, and causing ammonia water to act upon the obtained precipitate for partial demethoxylation and partially amidization in a state where the precipitate is substantially not dissolved.

2. A method for producing a pectin as set forth in claim 1, wherein the amount of the acid used for the demethoxylation is equivalent to or less than the amount of the acid required for extraction.

3. A method for producing a pectin as set forth in claim 1, wherein the acid used for the demethoxylation is an aqueous solution, the concentration of the solution is 0.1N or more, and the solution is used in amount not more than the weight of the plant in the dry state.

3. DETAILED DESCRIPTION OF THE INVENTION

[Field of Utilization in Industry]

The present invention relates to a method for producing a pectin. In further detail, it relates to a method for producing an amide type pectin comprising partially demethoxylating an ester portion of a partially methyl esterified D-galacturonic acid of a pectin and partially amidizing the same when extracting a pectin from a pectin-containing plant such as citrus peel.

The properties of pectins differ according to the degree of methoxylation of the D-galacturonic acid in the pectin molecule. Pectins having a degree of methoxylation of 50% or more are classified as high methoxy (HM) pectins, while those having a degree of methoxylation of less than 50% are classified as low methoxy (LM) pectins. Further, in HM pectins, the gelation speed differs according to the degree of methoxylation thereof, so these pectins are classified as a rapid set, a medium set, and a slow set according to the degree of methoxylation thereof. In LM pectins, the properties such as the hardness of the gel and elasticity differ according to the degree of methoxylation, so the adjustment of the degree of methoxylation is important for producing a pectin.

Further, LM pectins include two types, that is, LM pectins extracted by acid as they are and partially amidized LM pectins. The partially amidized pectins are characterized in that the optimum gelled calcium concentration range at the time of gelation by calcium is wide, so a good gel can be easily obtained, and further a gel having relatively high strength is easily obtained.

[Prior Art]

If producing a pectin without demethoxylation of the pectin, only a so-called rapid set HM pectin, for example, a pectin having a 70 to 75% degree of methoxylation with pectin extracted from peel of squeezed lemons or a pectin having a 67 to 72% degree of methoxylation with pectin extracted from peel of squeezed oranges, can be obtained. In order to obtain a pectin having the desired degree of methoxylation, it is necessary to perform the demethoxylation by an acid, alkali, or enzyme. When ammonia is used as the alkali at this time, partial amidation simultaneously occurs, whereby a partially amidized pectin is obtained.

As the method for producing a partially amidized LM pectin, there are a method of treating roughly prepared pectin obtained by extraction and precipitation in a usual pectin production process by a mixture of ammonia and an alcohol and a method of treating roughly prepared pectin by an acid-containing alcohol, then treating the same by a mixture of ammonia and an alcohol.

[Problems to be Solved by the Invention]

Among these methods, the former method require that demethoxylation be

carried out up to a degree required for performing the demethoxylation and the partial amidation at one stage, so it is necessary to raise the ammonia concentration and make the reaction time long. When performing the demethoxylation under such severe conditions, particularly in the presence of an alkali such as ammonia, the drop in the molecular weight, that is, the drop in the quality of the pectin due to cleavage of the glycoside bonds, cannot be avoided and in certain cases the product yield is also lowered.

In the latter case, the first state treatment method calls for reacting the obtained dehydrated precipitate with acid aqueous solution/alcohol of a volume ratio of about 1/1 to 1/2, a precipitate/acid-containing alcohol of a weight/volume ratio of about 1/1 to 1/3 and a concentration of acid with respect to the entire system of about 1 to 3N for several tens of hours. There is also a method of adding an alkali to the system to neutralize it at the end of this reaction, but if using such a method, since the acid concentration is high, a large amount of the alkali is also required for the neutralization. Even if pressing and drying the precipitate, a large amount of salt such as about 20% remains in the product and consequently lowers the quality of the product. In order to avoid this, usually, when ending the reaction, use is made of a method of repeatedly washing the reaction system by alcohol containing water to remove the excess acid. It is necessary to treat the thus obtained precipitate by a mixture of ammonia and an alcohol and wash it again in the same way as the former method, so there are the problems that the operation becomes complex, the equipment becomes complex, and the amount of usage of the alcohol increases, so the cost becomes high.

The present invention provides a method for producing a partially amidized pectin free from such problems and having a high efficiency.

[Means for Solving the Problem]

The gist of the present invention resides in a method for producing a partially amidized pectin comprising causing a pectin-containing plant in a dry state to swell by an acid to partially demethoxylate the pectin, then dissolving the pectin and separating the insolubles, then causing the pectin to precipitate, and causing ammonia water to act upon the obtained precipitate for partial demethoxylation and partially amidization in a state where the precipitate is substantially not dissolved. an the weight of the plant in the dry state. Namely, it resides in the method of treating a pectin-containing plant by an acid to lower the degree of methoxylation, separating the pectin, then further demethoxylating the pectin by ammonia and, at the same time, amidizing it.

As the acid used in the present invention, preferably use is made of an organic acid such as hydrochloric acid, sulfuric acid, and nitric acid. Also, an organic acid such

as acetic acid and citric acid can be used, but these have the defect that the yield becomes low.

The demethoxylation by the acid is carried out by adding the acid to the pectin-containing plant in the dry state. Preferably the concentration of the added acid is 0.1N or more. When lower than this, the time required for the reaction becomes long. Any method such as spraying or blending by a blender can be employed as the method of addition of the acid, but it is particularly preferable to exercise care so as to homogeneously mix the acid and the plant.

The acid acts as a catalyst in the demethoxylation, so the amount of the acid is not particularly limited, but it is preferably used in about 0.5 to 2.0 grams equivalent weight with respect to 1 kg dry weight of the plant. It is preferable not to remove the acid used in the demethoxylation as it is, but if necessary further adding acid and adding water to adjust the concentration for extraction, whereby the same acid can be used for both the demethoxylation and the extraction. The amount of the acid used for the demethoxylation may become larger than the amount of the acid used for the extraction, but when it exceeds the amount of the acid used for the extraction, partial washing or neutralization becomes necessary before the extraction. Accordingly, preferably the amount of the acid used for the demethoxylation is equivalent to or less than the amount of the acid required for the extraction. Further, preferably use is made of the acid aqueous solution for the demethoxylation in an amount that becomes the weight of the plant in the dry state or less. This is because the present inventors found the fact that, when the amount of the water unnecessarily became large with respect to the required acid, the concentration of the acid was lowered and the reaction time became long, therefore preferably the amount of the aqueous solution was not more than the weight of the plant in the dry state considering both of the facility of homogeneous mixing and the reaction time. Even if concentrated acid is used, so long as the homogeneous blending can be carried out, there is no particular problem, so there is no upper limit on the acid concentration. For example, when using the spraying method, relatively concentrated acid can be used. After the plant is impregnated with the acid, preferably the reaction system is sealed during the demethoxylation reaction so as not to allow a change in the concentration due to the evaporation of moisture etc. In order to adjust the degree of methoxylation of the pectin to the desired value in the first stage, the reaction time of the demethoxylation, the concentration of the acid, the amount of the acid, the reaction temperature, etc. may be appropriately adjusted.

In the treatment by the ammonia water, it is necessary to perform the treatment in a state where the precipitate is not substantially dissolved. Namely, preferably the

treatment is carried out by using a mixed solution of the aqueous ammonia solution and a water miscible organic solvent. The volume ratio between the aqueous ammonia solution and the water miscible organic solvent is preferably 1/1 to 1/2, and the weight/volume ratio between the precipitate and the mixed solution is 1/1 to 1/3. The concentration of the ammonia with respect to the entire system is preferably about 0.5 to 1.5N. Under such conditions, the required reaction time at room temperature may be about 30 minutes to a few hours. When the ammonia concentration of the system is too low, a long time is required for the reaction, so this not preferred, while when it is too high, the reaction speed is too fast, so control becomes difficult.

[Examples]

Below, a detailed explanation will be given of the present invention by using examples.

Note that, in the examples, the degree of methoxylation and the degree of the amidation were according to the method disclosed in the *Food Chemicals Codex*, 3rd edition. Further, the strength of gel was measured by preparing a reaction system having a gel composition of a sugar degree of 31%, a pH of 3.0, 1% of pectin, and 250 mg/kg of calcium, and using a neocadometer.

Example 1

1 liter of a 1N hydrochloric acid aqueous solution was added to 3.0 kg of dried peel of squeezed lemons and mixed. The peel swelled due to this aqueous solution. This was placed in a polyethylene bag and sealed, then allowed to stand at 25°C for 72 hours. After a while, the peel was placed in an extraction tank, water was added to 100 liters, the temperature was raised, and the mixture was stirred and extracted at 90°C over 30 minutes. The pH of the extract was 2.0. Next, the insolubles were removed by centrifugal separation, and 400 g of a diatomaceous earth filter aid was added to the obtained supernatant which was then filtered under pressure to thereby obtain 7.8 kg of a clear filtrate. Isopropyl alcohol was added to this filtrate to a 60 vol% concentration, and the precipitate of the precipitated pectin was separated and pressed to thereby obtain 2.4 kg of a precipitate having a solids concentration of 25%. 4.4 liters of isopropyl alcohol having a 60 vol% concentration and 400 ml of 25% ammonia water were added to this precipitate. The result was mixed by stirring and reacted for 3 hours. Then, the pH was controlled to 4.0 by concentrated hydrochloric acid, and the precipitate was separated and pressed. An amount of isopropyl alcohol two times the amount of the precipitate was added to this precipitate, the salt contained in the precipitate was dissolved, then the precipitate was separated and pressed again, then dried and crushed to thereby obtain 58 g of a pectin powder. The degree of methoxylation of the obtained

pectin was 30.0%, and the degree of the amidation was 16.3%. Further, the strength of the gel was 163 g/cm². Note that the degree of methoxylation before the ammonia treatment was 57.1%.

Example 2

1550 ml of a 2.3N hydrochloric acid aqueous solution was added to 3.0 kg of dried peel of squeezed oranges and mixed. The peel swelled due to this aqueous solution. This was placed in a bag made of polyethylene and sealed and allowed to stand at 30°C for 20 hours. After this, the same treatment as that in Example 1 was carried out to obtain a pectin powder except for using 4 liters of isopropyl alcohol having a 60 vol% concentration and 270 ml of 25% ammonia water in the ammonia water treatment. Note that the pH at the time of the extraction was 2.1. The degree of methoxylation of the obtained pectin was 36.4%, and the degree of the amidation was 12.0%. Further, the strength of the gel was 148 g/cm². Note that the degree of methoxylation before the ammonia treatment was 52.3%.

Comparative Example 1

The same procedure was followed as in Example 1 to produce pectin from 3.0 kg of dried peel of squeezed lemons except for not causing the dried peel to swell by an acid aqueous solution in advance and in that state sealing and allowing the peel to stand and making the conditions after the extraction the use of 4 liters of isopropyl alcohol having a 60 vol% concentration and 450 ml of 25% ammonia water in the ammonia water treatment. The degree of methoxylation of the obtained pectin was 28.6%, and the degree of the amidation was 20.3%. Further, the strength of the gel was 124 g/cm². A pectin is usually used as a compound added with a cheap diluent such as sugar or grape sugar, but if adding a diluent, the strength of the gel is lowered. This compound needs a predetermined strength of the gel in accordance with the purpose thereof. A compound having a required strength of the gel cannot be obtained by a pectin having a strength of the gel such as 124 g/cm², or even if it can be obtained, almost no diluent can be added, therefore the cost of the compound becomes high, so it becomes economically disadvantageous.

[Effect of the Invention]

As apparent from the above examples, the invention of the present application comprising treating a pectin-containing plant by an acid in advance, separating the pectin, then treating the same by ammonia has the excellent effects that it can give a high quality pectin, no excess drop in the molecular weight of the pectin as in the prior art is induced, the washing of the salt generated by the neutralization after that is relatively easy, and so on. Further, the methoxylation can be adjusted by the acid used

for the extraction, so the method is economical.